MAGNESIAN HALOTRICHITE FROM VINTON COUNTY, OHIO

RUSSELL A. BRANT AND WILFRID R. FOSTER

Ohio Division of Geological Survey and Department of Mineralogy, Ohio State University, Columbus

During the Fall of 1956 and Spring of 1957, a study was made of acid waters issuing from abandoned coal mines located in the upper part of Sandy Run Valley tributary to Lake Hope (fig. 1). This study was part of a broader one of acid mine water pollution made under the direction of The Ohio State University Engineering Experiment Station. It was during this time that white efflorescences were found and that interest in their particular nature began. The following report is 1) a general description of the site geology where the mineral was found, 2) a description of the mineral and comparison with others of the general nature, and 3) notes on the origin of the mineral Halotrichite.

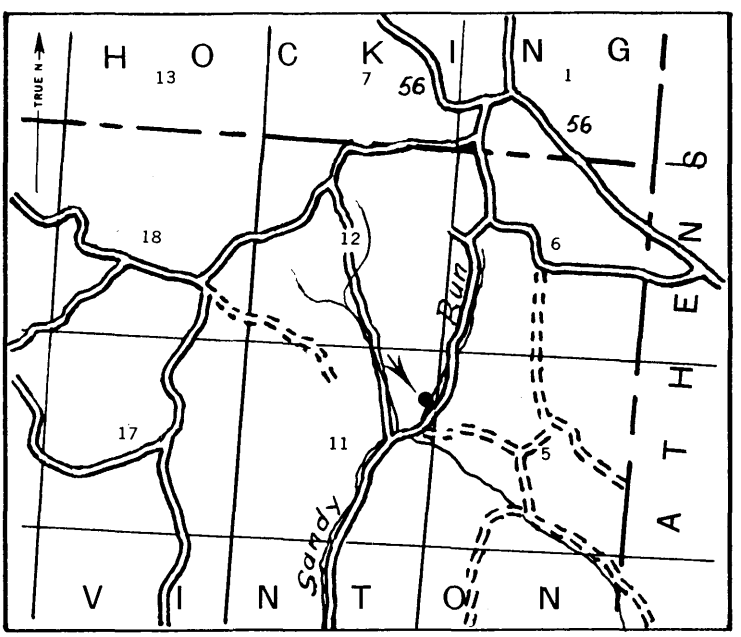

FIGURE 1. Location map of the northeast part of Brown Township, Vinton County. Arrow and dot indicate the location of the abandoned mine were the halotrichite was found.

Site Geology

In the watershed area of Lake Hope the surface is underlain by rocks of the Allegheny and the lower Conemaugh series of the Pennsylvanian system. In this area several coal and clay beds of commercial thickness occur, and in the upper part of Sandy Run Valley the Middle Kittanning coal has been extensively mined. The Lower Freeport sandstone overlies the coal. In this area its occurrence is massive and is associated with the overlying similar Upper Freeport sandstone. These form steep valley walls or cliff faces.

In some places undercutting of the Lower Freeport sandstone, by removal of the Middle Kittanning coal and clay and partly by removal of the lower portion of the sandstone, has produced hollows or overhang ledges. At the mineral

location the coal outcrop occurs beneath the overhanging ledge and two mine entries have been made into the coal (fig. 2). Water issues from one opening and some of it flows into other abandoned workings. On piles of loose material formed from mine refuse as well as spall material from the sandstone, a white efflorescent mineral was found.

Mineralogy

The Vinton County mineral (fig. 3) was first thought to be alunogen, a hydrated aluminum sulfate with the formula $Al_2(SO_4)_3 \cdot 18H_2O$. The mode of occurrence, fibrous habit, alumlike taste, water-solubility, and observable optical properties are all consistent with such an identity. Furthermore, a recently reported occurrence of alunogen under somewhat similar conditions in West Virginia would seem to support this tentative identification (Temple and Koehler, 1954). However, chemical analysis and x-ray diffraction data did not bear out this conclusion.

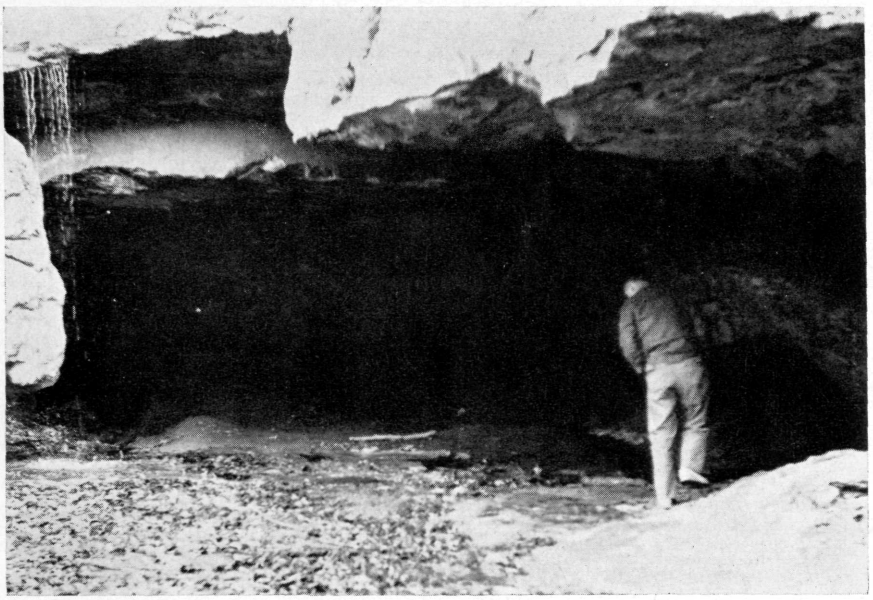

FIGURE 2. Site of halotrichite occurrence at opening of rock overhang near mine opening. White area in right foreground is a deposit of halotrichite lying on spall from the rock overhang.

The first suggestion that the mineral was not alunogen came from an examination of its x-ray diffractometer pattern as well as from concurrent chemical data. The x-ray data did not even approximately fit the data for alunogen, as recorded on card 1–0348 of the A.S.T.M. card file of x-ray diffraction data. Chemical analysis strongly suggested that the mineral might be a member of the pickeringite-halotrichite series, the end-member formulas of which are $MgAl_2(SO_4)_4 \cdot 22H_2O$ and $FeAl_2(SO_4)_4 \cdot 22H_2O$, respectively. Comparison of its x-ray diffraction pattern with that of pickeringite from New Mexico, and with recently published data for halotrichite from White Mountain, California (Baur and Sand, 1957) left little doubt that the Vinton County material was a member of this series. In figure 4 the patterns of pickeringite and halotrichite are practically undistinguishable, attesting to the difficulty of distinguishing between end-members or intermediate members of the series without resorting to chemical analysis. The correspondence of the

mineral alunogen with reagent-grade aluminum sulfate is also clearly shown. So-called alunogenite from West Virginia corresponds to the pickeringite and halotrichite patterns, rather than to alunogen.

In table 1 chemical analyses of the Ohio mineral and the California halotrichite are compared to the pure theoretical iron end-member of the series. The similarity between the last three columns is apparent. The analysis of the Vinton County material suggests that magnesia substitutes for a portion of the iron oxide; the mineral would, therefore, properly be called magnesian halotrichite.

The principal optical properties of pickeringite, halotrichite, and alunogen, as recorded in the widely-used determinative tables of Larsen and Berman (1934) are compared in table 2.

Because of the finely fibrous nature of these minerals, certain properties such as optic sign, which might serve to distinguish pickeringite-halotrichite members from alunogen, cannot readily be determined. Table 2 leaves little doubt as to

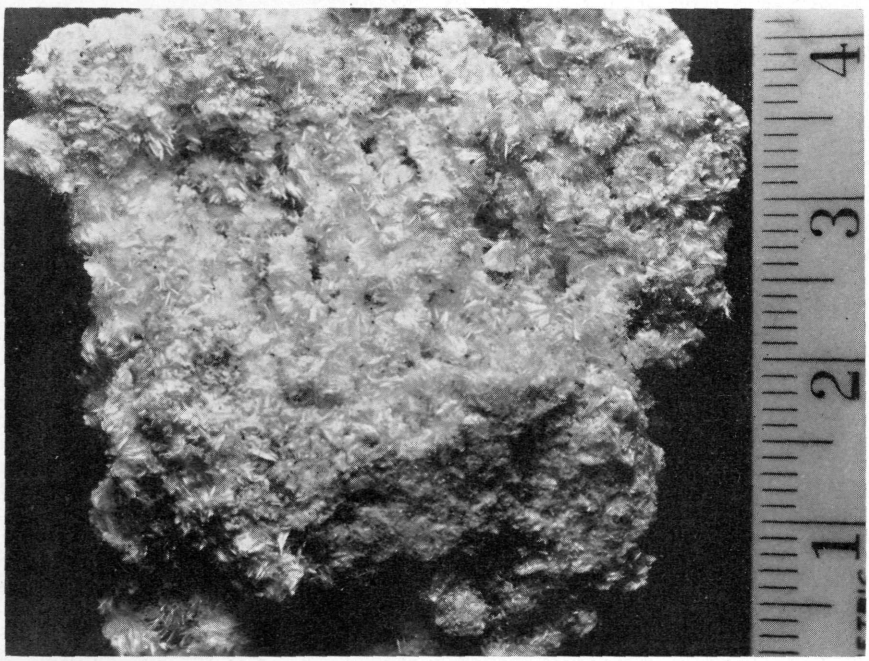

FIGURE 3. Detail of halotrichite mass showing fibrous nature.

the difficulties involved in conclusive distinction between these various minerals on the basis of optical properties alone. It is, therefore, highly probable that halotrichite and pickeringite are often erroneously identified as alunogen, particularly if the determination has relied primarily upon optical examination. At least three such instances are known to the authors. Thus, a sample from the United States National Museum labelled "alunogen" was demonstrated by x-ray diffraction to be a member of the pickeringite-halotrichite series. The "alunogenite" sample from West Virginia (fig. 4) is likewise a member of the series; so also is a sample from Nevada which had been microscopically identified as "alunogen." Northrup (1942) has observed that halotrichite is apparently exceedingly rare in the United States. He suggests, however, that it is perhaps more common than the records would indicate. Our experience would tend to substantiate this latter statement.

As a corollary to the above described occurrence, a coal core, stored in a basement for approximately four years, was examined. The conditions were not unlike those of some coal mines. Over much of the surface of this core was a deposit of feathery clusters, many of which had become detached and formed a fluffy aggregate between the core and the enclosing box. The deposit proved to be halotrichite. All of the cluster areas noted were points at which appeared small blebs of pyrite or marcasite about 1 mm by 5 mm in dimension. However, in a zone about 1 ft from the base of the coal, the site of a sulphide lens was noticed about 2 in. in thickness. At this place was an occurrence of melanterite, as nearly colorless transparent crystal fragments with a bluish green cast. That both minerals are formed under somewhat similar circumstances is interesting to note.

TABLE 1
Chemical composition

Chemical constituent	$MgAl_2(SO_4)_4 \cdot 22H_2O$ (Theoretical)	Halotrichite Vinton Co. Ohio	Halotrichite White Mountains California	$FeAl_2(SO_4)_4 \cdot 22H_2O$ (Theoretical)
MgO	4.69	2.7	——	——
FeO	——	5.9	6.8	8.07
MnO	——	0.4	——	——
CaO	——	0.4	——	——
Al_2O_3	11.87	12.3	12.0	11.45
SO_3	37.29	39.3	37.1	35.97
H_2O	46.15	38.8	43.8	44.51

TABLE 2
Optical properties

	Pickeringite	Halotrichite	Alunogen
Alpha	1.476	1.480	1.474
Beta	1.480	1.488	1.476
Gamma	1.483	1.490	1.483
Axial angle	Medium	Medium small	69°
Optic sign	Negative	Negative	Positive
Orientation	Y=b	Y=b	X=b
System and Habit	Z C=37° Mon. Fib.	Z C=38° Mon. Fib. C	Z C=42° Mon. Tab. (010) Fib. C
Color	Colorless, yellow, reddish	Colorless	White

Origin of Halotrichite

The source of the sulfate radical which makes up an essential part of the composition of halotrichite is a matter of considerable interest. Several possible origins have been proposed, and well-substantiated examples of each have been described. One proposed mode of origin involves volcanic action, the sulfate emanating from hot ascending gases or solutions associated with fumaroles or hot springs. Of such origin are the primary sulfates of Gila River, New Mexico, the hot spring deposits (Hayes, 1907) at Lassen Peak, California, and the solfataras near Naples, Italy.

A more common source of such sulfates is the oxidation of pyrite or marcasite disseminated through ore deposits, sedimentary rocks, or coal seams. An early view maintained that the oxidation of pyrite could not lead to the production

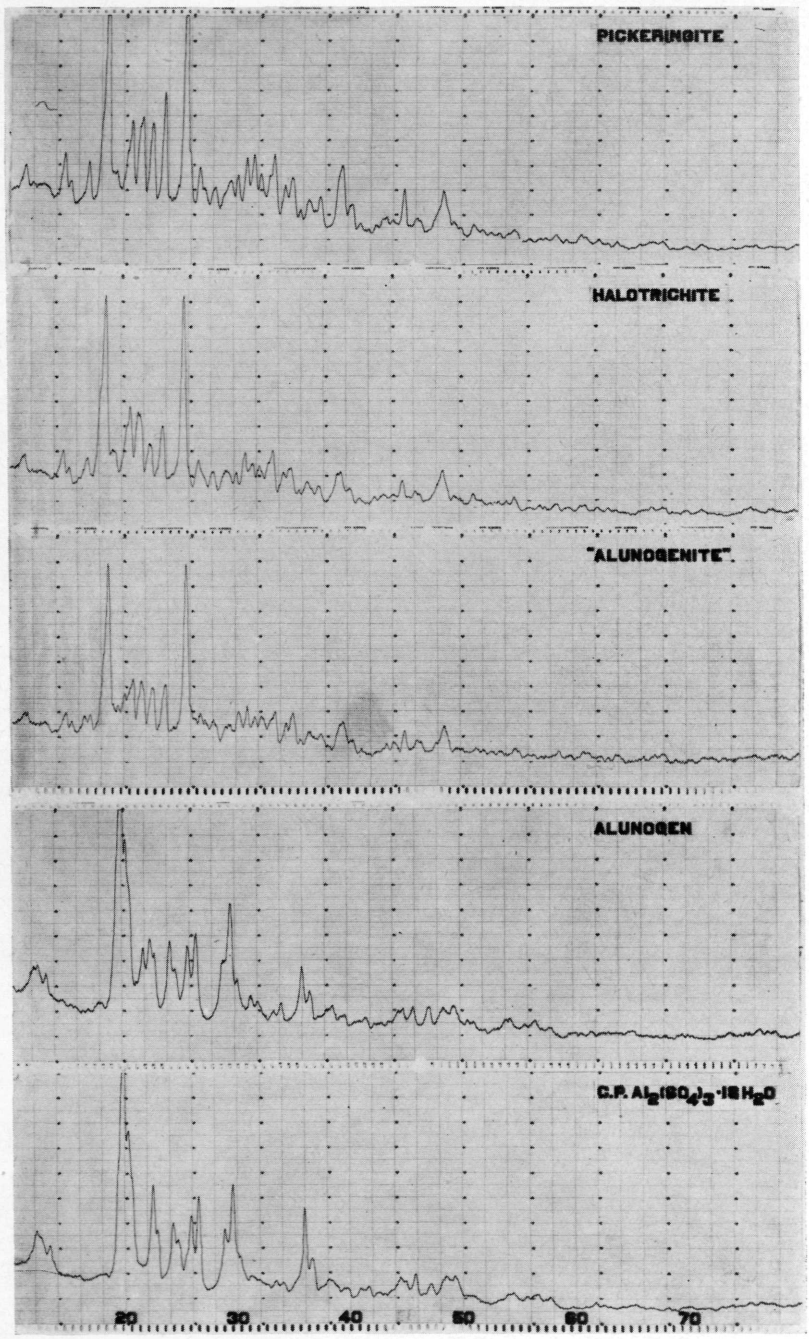

FIGURE 4. Comparison of x-ray diffractometer curves of pickeringite, halotrichite, "alunogenite," alunogen, cp $Al_2(SO_4)_3 \cdot 18H_2O$. Sources of material are listed in table 3.

of a ferrous-iron mineral such as halotrichite (Hayes, 1907). This view no longer appears to be tenable. Bandy (1938) attributes the halotrichite of the sulfate deposits of northern Chile to the direct oxidation of pyrite. Palache, Berman, and Frondel (1957) state that pickeringite and halotrichite are commonly formed as the products of weathering of pyritic rocks. Such weathering also furnishes ample iron, and there is no dearth of readily available alumina in the clay minerals and feldspars of the most common types of sedimentary and igneous rocks.

Whatever may be the ultimate source of the sulphate, there seems little doubt that the actual deposition of halotrichite is merely a matter of evaporation of an aqueous solution of ferrous and aluminum sulfates with or without an excess of sulphuric acid. Laboratory studies have demonstrated that such a process leads to its formation (Occleshaw, 1925). Capillary action draws such solutions through porous or fractured rock formations, and surface evaporation of the water causes the deposition of halotrichite. Favorite sites for the accumulation of such deposits

TABLE 3

Source of samples used for x-ray patterns

Specimen	Locality	Donor
Pickeringite	San Miguel Co., Colorado	U. S. Nat. Museum (No. 95410)
Halotrichite	Vinton Co., Ohio	Ohio Geological Survey
"Alunogenite"	Monongalia Co., W. Va.	W. Va. Experiment Sta.
Alunogen	Chacance, Chile	U. S. Nat. Museum (No. C 5576)
$Al_2(SO_4)_3 \cdot 18H_2O$	Chemical Reagent	Baker and Adamson

are the walls, ceilings, and floors of tunnels and caves, and the undercut sides of overhanging cliffs. Such sheltered places are conducive to the deposition of layers and encrustations of this highly soluble mineral while protecting it from the subsequent solvent action of rain water. Arid regions are, therefore, particularly favorable for such accumulations.

The genesis of the Vinton County halotrichite is believed to be somewhat as follows: the oxidation of pyritic material forms sulphate ions in place which may unite with iron, aluminum, and other ions to form the salt halotrichite. Upon dissolving, the compound may later reappear as a new deposit in protected and suitable sites as mentioned above. Mine waters, containing relatively high sulphuric acid and an assemblage of other ions from various sources, may conceivably be associated in a capillary situation to feed a desiccation surface of porous material and to allow the accumulation of the salt.

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